



(11) **EP 1 009 047 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 158(3) EPC

(43) Date of publication:
14.06.2000 Bulletin 2000/24

(51) Int. Cl.⁷: **H01M 4/66**, H01M 4/02,
H01M 4/04, H01M 10/40

(21) Application number: 99922545.1

(86) International application number:
PCT/JP99/02828

(22) Date of filing: 27.05.1999

(87) International publication number:
WO 99/62133 (02.12.1999 Gazette 1999/48)

(84) Designated Contracting States:
DE FR GB

(30) Priority: 28.05.1998 JP 14711798

(71) Applicant:
MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD.
Kadoma-shi, Osaka 571-8501 (JP)

(72) Inventors:
• **HASHIMOTO, Tatsuya**
Itami-shi Hyogo 664-0874 (JP)
• **MURAI, Hiroyuki**
Hirakata-shi Osaka 573-1152 (JP)

• **OHANA, Yorihiro**
Hirakata-shi Osaka 573-0005 (JP)
• **MATSUNO, Hiroshi**
Moriguchi-shi Osaka 570-0008 (JP)
• **ASANO, Hideya**
Hirakata-shi Osaka 573-1104 (JP)

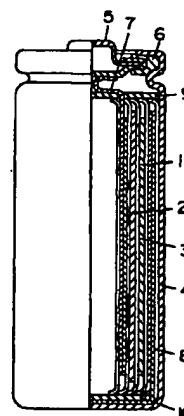
(74) Representative:
Butcher, Ian James et al
A.A. Thornton & Co.
235 High Holborn
London WC1V 7LE (GB)

(54) **BATTERY PLATE AND BATTERY**

(57) What is made available by the present invention is a battery, in which measures are taken to suppress a reduction in charge/discharge capacity and degradation of load characteristics due to peeling of an active material off the current collector during the use of the battery with charge/discharge operations repeated. An application of a boehmite treatment or a chromate treatment to the current collector surface of the electrode plate for the battery makes it possible for the degradation of charge/discharge capacity and load characteristics to be suppressed to a minimum.

Fig 1

1. Electrode Plate for Positive Electrode
2. Electrode Plate for Negative Electrode
3. Separator
4. Battery Case
5. Sealing Plate
6. Gasket
7. Positive Electrode Lead
8. Negative Electrode Lead
9. Upper Insulating Plate
10. Lower Insulating Plate



EP 1 009 047 A1

Description

FIELD OF THE INVENTION

5 [0001] The present invention relates to improvements in electrode plates for battery and a battery using the improved electrode plates for battery.

BACKGROUND OF THE INVENTION

10 [0002] In order to prevent falling of an active material off a current collector of a battery due to usage of repeated charge/discharge operations or during the assembly work of batteries, an application of a chromate treatment or a corona discharge treatment to the surface of the current collector has so far been proposed. (The Japanese Patent Unexamined Publication Nos. S56-57261 and H7-135023) Also, relative to the manufacturing of electrode plates for a lithium-ion secondary battery, a method of performing dispersion by kneading under the presence of a surface-active agent is disclosed as the method for improving the wettability of an active material against a bonding agent and a viscosity improver. (The Japanese Patent Unexamined Publication No. H8-190912)

15 [0003] However, it is found difficult for the foregoing electrode plates for battery to achieve an improvement in wettability of an active material against a bonding agent and a viscosity improver and also to satisfy the required adhesiveness between a current collector and an active material after the active material has been applied to the current collector. As a result, after a storage under high temperatures or during repeated charge/discharge operations, the active material peels and falls off the current collector, thereby causing the problem of a reduction in charge/discharge capacity.

20 [0004] The present invention deals with the foregoing unsettled problem to realize a lithium-ion secondary battery which shows minimal corrosion of a current collector due to an active material, minimal peeling and falling of the active material off the current collector, thereby demonstrating large discharge capacity.

DISCLOSURE OF THE INVENTION

30 [0005] The present invention deals with the afore-mentioned problem to provide an electrode plate for battery and a battery using it, the electrode plate for battery being characterized by applying a boehmite treatment to the surface of a current collector prior to an application of a paste, which is formed of a composition with an active material acting as the principal ingredient, to the current collector.

35 [0006] With a method for producing electrode plates for lithium secondary battery characterized by applying a paste containing a positive electrode active material to a current collector formed of a metallic foil and then drying the paste, the current collector is applied with a chromate treatment on the surface thereof to form a chrome oxide layer prior to the foregoing application of the paste.

[0007] The present invention discloses a method for producing electrode plates, the method comprising the steps of:

40 applying a boehmite treatment to the surface of current collector of one electrode plate selected from a positive electrode plate and a negative electrode plate or applying a chromate treatment to the surface of a positive electrode current collector;
applying a paste formed of a composition containing an electrode active material on the current collector; and
45 drying the paste.

Even when a battery employing the electrodes as described in the above is in usage with repeated charge/discharge operations, a reduction in the charge/discharge capacity and degradation in the load characteristics can be suppressed to a minimum.

50 BRIEF DESCRIPTION OF THE DRAWINGS

[0008]

55 Fig. 1 is a cross-sectional view of a battery in an exemplary embodiment of the present invention.
Fig. 2 is a diagram to show cycle life characteristics by making a comparison between a prior art battery and a battery in an exemplary embodiment of the present invention.
Fig. 3 is a diagram to show cycle life characteristics by making a comparison between a prior art battery and a battery in another exemplary embodiment of the present invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0009] Next, a description is given to a case where a boehmite treatment is applied to a positive electrode current collector for lithium-ion battery in an exemplary embodiment of the present invention.

(First Exemplary Embodiment)

[0010] A lithium-ion secondary battery in an exemplary embodiment of the present invention is a cylindrical lithium-ion secondary battery as shown in Fig. 1 and formed of a group of electrode plates produced according to the method as disclosed by the present invention, an electrolyte and a battery case 4 accommodating the foregoing. The group of electrode plates includes a sheet like electrode plate 1 for positive electrode, a sheet like electrode plate 2 for negative electrode, a sheet like separator 3 insulating the electrode plate 1 for positive electrode from the electrode plate 2 for negative electrode, a positive electrode lead 7, a negative electrode lead 8, an upper insulating plate 9 and a lower insulating plate 10. The separator 3 is a porous polyethylene film. All of the foregoing elements are superimposed one over another, wound in a spiral fashion and placed inside the cylindrical battery case 4.

[0011] The battery case 4 is prepared by applying a deep drawing process to a stainless steel sheet having resistance to an organic electrolyte. After the group of electrode plates and electrolyte have been placed inside the battery case 4, the opening of the battery case 4 is closed by sealing with a sealing plate 5 and a gasket 6 that acts as an insulator and also applies gas sealing between the sealing plate 5 and the battery case 4.

[0012] Now, a description is given to a boehmite treatment. After a 30 μm thick aluminum foil acting as a positive electrode current collector has been immersed in a 12 cc/l solution of triethanolamine, an oxide film is formed by drying the foregoing aluminum foil for 4 hours at 100 °C to have the surface of the aluminum foil reformed. At this time, the thickness of the oxide film is preferred to be 0.5 to 5.0 μm . When the thickness of the oxide film is smaller than 0.5 μm , a sufficient effect of reforming the surface of the aluminum foil is not allowed to be realized, resulting in not so excellent adhesion with an active material. On the other hand, when the thickness of the oxide film exceeds 5.0 μm , the amount of the active material, which is allowed to be contained in the given same size of the battery case 4, is reduced, resulting in an excessive reduction of the battery capacity to cause an unacceptably large adverse effect.

[0013] Next, a description is given to a method for producing the electrode plate 1 for positive electrode. A paste formed of composition with an active material for positive electrode serving as the principal ingredient is prepared by mixing/dispersing 50 weight parts LiCoO_2 powder as the positive electrode active material, 1.5 weight parts acetylene black as a conductive agent, 7 weight parts aqueous solution of 50 weight parts PTFE as a binder and 41.5 weight parts aqueous solution of 1 weight part carboxymethylcellulose as a viscosity improver. The paste for positive electrode thus prepared is applied to both surfaces of the boehmite treated aluminum foil by using a die coater and, after the coated paste has been dried, the aluminum foil applied with the paste is heated to the melting temperature of PTFE ranging 200 °C to 300 °C, thereby further improving the adhesion between the current collector and the positive electrode composition layer. Then, the aluminum foil is rolled to a thickness of 0.18 mm and cut to produce the sheet like electrode plate 1 for positive electrode of the present invention.

[0014] A description is given to a method for producing the electrode plate 2 for negative electrode. A paste for negative electrode is prepared by mixing/dispersing 50 weight parts powder of scale like graphite particles acting as the negative active material, 45 weight parts aqueous solution prepared by dissolving 1 weight part carboxymethylcellulose in 99 weight parts water to form a viscosity improver and 5 weight parts styrene-butadiene-rubber as a binder. The paste thus prepared is applied to a 40 μm thick copper foil by using a die coater to produce the electrode plate 2 for negative electrode.

[0015] The electrolyte is prepared by dissolving LiPF_6 in a mixed solution of 30 vol% ethylene carbonate, 50 vol% diethyl carbonate and 20 vol% methyl propionate to a concentration of 1 mol/l. This electrolyte is contained inside the battery case, in which the positive electrode active material layer and negative electrode active material layer are impregnated with the electrolyte, thereby causing a cell reaction to take place with the electrolyte serving as a carrier of lithium ions between the electrode plate 1 for positive electrode and the electrode plate 2 for negative electrode by passing through minute holes of the porous separator 3.

[0016] A battery is prepared by using the foregoing electrode plate 1 for positive electrode and cycle characteristics of the battery are checked. The battery thus prepared measures 17 mm in diameter and 50 mm in height.

[0017] A battery for comparison, which is the same as the foregoing battery of the present invention except for using a positive electrode current collector with no boehmite treatment applied to the surface thereof, has been prepared to carry out a side-by-side performance evaluation.

[0018] The battery of the present invention and the battery for comparison are subjected to a cycle test, one cycle of which comprises the steps of constant current charging at 500 mA until the battery voltage reaches 4.1 V, switching to constant voltage charging when the battery voltage reaches 4.1 V, continuing the constant voltage charging until the total charging time reaches 2 hours, starting discharging at 720 mA in an ambient temperature of 20 °C and suspending

the discharging when the discharge voltage decreases to 3.0 V. Upon completing one cycle as above, the next cycle is started. Fig. 2 shows the results of the cycle test i.e., cycle life characteristics, on the foregoing battery of the present invention and the battery for comparison with a capacity maintenance ratio indicated on the vertical axis and a number of cycles on the horizontal axis when charge/discharge operations as described in the above are repeated. It is found out from Fig. 2 that the battery of the present invention shows little degradation in capacity after repeated charge/discharge operations when compared with the battery for comparison, thereby proving that the battery of the present invention has excellent cycle characteristics.

[0019] This is because of the needle like structure formed on the surface of the positive electrode current collector by an application of a boehmite treatment thereto and the enhanced adhesion between the current collector and the composition layer with the active material acting as the principal ingredient, the enhanced adhesion having been realized by the polymeric material of PTFE entangled with the needle like structure in a three-dimensional manner to demonstrate an anchor effect. Therefore, even when the composition layer containing the active material expands/shrinks due to repeated charge/discharge operations, it is hard for the composition layer to get separated from the current collector.

[0020] Also, the battery of the present invention and battery for comparison are kept in storage under a charged condition for 20 days at 60 °C and then subjected to several times of repeated charge/discharge operations at room temperature, followed with a discharging operation at 720 mA to find capacity till the time when the battery voltage reaches 3.0 V. The resulting capacity is compared with the capacity just before being kept in storage and Table 1 shows the findings.

Table 1

High Temperature Storage Characteristics	Battery of Present Invention	Battery for Comparison
(Capacity after Storage/Capacity before Storage) × 100 (%)	98	93

[0021] As shown in Table 1, the battery of the present invention is found to show little degradation in capacity even under a high temperature storage condition.

[0022] A case, where the boehmite treatment is applied to the positive electrode current collector for a lithium secondary battery, is shown in the present exemplary embodiment but the boehmite treatment is also allowed to be applied to the negative electrode current collector for the same effect, and further the same effect can be gained even when the boehmite treatment is applied to electrode plates of other battery systems.

(Second Exemplary Embodiment)

[0023] The preparation of an electrode plate 1 for positive electrode is made in the same way as in the first exemplary embodiment except for using an aluminum foil, on the surface of which a chromium oxide layer is formed in advance by a chromate treatment, in place of an aluminum foil that is boehmite treated.

[0024] A paste for negative electrode used with an electrode plate 2 for negative electrode is prepared according to the same method as employed in the first exemplary embodiment. The obtained paste for negative electrode is applied to both surfaces of a negative electrode current collector formed of a 50 µm thick copper foil by using a die coater and the applied paste is dried. Then, the copper foil is rolled to a thickness of 0.2 mm and cut to produce a sheet like electrode plate 2 for negative electrode.

[0025] An electrolyte, which is the same one as used in the first exemplary embodiment, is used in the present exemplary embodiment.

[0026] A battery is produced by using the foregoing electrode plate 1 for positive electrode in the same way as the first exemplary embodiment and the cycle characteristics of the battery are checked. The battery thus produced measures 17 mm in diameter and 50 mm in height.

[0027] As a battery for comparison is used a lithium secondary battery prepared according to the same method as employed in the first exemplary embodiment except for using a positive electrode current collector without applying any chromate treatment to the surface thereof. Then, a comparison is made between the battery for comparison of above and a lithium secondary battery using the positive electrode plate prepared according to the method of the present invention and the cycle characteristics of both batteries are as shown in Fig. 3.

[0028] In the same way as in the first exemplary embodiment, the batteries are charged with a constant current of 500 mA and then, when the battery voltage has reached 4.1 V, charging of the batteries is switched to constant voltage charging, the constant voltage being 4.1 V, with the total charging time extended to as long as 2 hours. Discharging of the batteries is performed with a discharge current value of 720 mA at 20 °C and, when the discharge voltage has

reached 3.0 V, the discharge cycle is ended and a new charge cycle is started. What is found out from Fig. 3 is that the lithium secondary battery using the electrode plate for positive electrode produced according to the method of the present invention shows little degradation in capacity in comparison with a lithium secondary battery using the electrode plate for positive electrode prepared according to the conventional method even when a charge/discharge operation is repeated, thus demonstrating excellent cycle characteristics.

[0029] This is because of the following reason. The battery using the electrode plate for positive electrode of a lithium secondary battery prepared according to the production method of the present invention shows a reduction in corrosion of the current collector caused by a composition layer since the composition layer with the principal ingredient thereof formed of an active material does not come into a direct contact with the current collector although the surface of the positive electrode current collector is chromate treated and the chromate treated coating on the surface of the current collector is corroded, and further since generation of hydrogen gas, which takes place in the vicinity of an interface between the two different substances at the time of corrosive reaction, can be suppressed, the adhesion between the positive electrode composition layer and the current collector is enhanced, thereby making it hard for the positive electrode composition layer to peel off from the current collector even if the positive electrode composition layer undergoes expansion/shrinkage due to charge/discharge operations of the battery.

[0030] In addition, when an aluminum foil is used to form the positive electrode current collector, the surface of the aluminum foil is corroded moderately by the chromate treatment applied thereto, thereby enhancing markedly the adhesion of the positive electrode composition layer to the current collector because of the anchor effect created on the surface of the aluminum foil. On the other hand, when an iron foil is used to form the current collector, the anchor effect due to the chromate treatment is small.

[0031] Lithium secondary batteries prepared by the use of these electrode plates for positive electrode are kept in storage under a charged condition for 20 days at 60 °C, and then subjected to several times of repeated charge/discharge operations at room temperature, followed with a discharging operation at 720 mA to find capacity till the time when the battery voltage reaches 3.0 V. The resulting capacity is compared with the capacity just before being kept in storage and Table 2 shows the findings.

Table 2

High Temperature Storage Characteristics	Battery of Present Invention	Battery for Comparison
(Capacity after Storage/Capacity before Storage) × 100 (%)	99	93

[0032] As shown in Table 2, a lithium secondary battery using an electrode plate for positive electrode prepared according to the production method of the present invention is found to show little degradation in capacity even under a high temperature storage condition.

INDUSTRIAL USABILITY

[0033] As described in the above, the present invention makes it possible for a secondary battery to suppress the degradation in charge/discharge capacity and storage characteristics to an extremely small extent when the battery is used in repeated charge/discharge operations.

In addition, even under such a stringent condition as the battery is in storage at high temperatures for a long period, the degradation in charge/discharge capacity can be suppressed to a minimum. Also, a composition layer formed of an active material acting as the principal ingredient thereof is prevented from peeling off the current collector of an electrode plate during the assembly work of batteries, thereby enabling the enhancement of workability involved with the assembly work of the batteries.

Key to Reference Numerals

[0034]

1. Electrode Plate for Positive Electrode
2. Electrode Plate for Negative Electrode
3. Separator
4. Battery Case
5. Sealing Plate
6. Gasket

7. Positive Electrode Lead
8. Negative Electrode Lead
9. Upper Insulating Plate
10. Lower Insulating Plate

Claims

1. An electrode plate for battery characterized by using a current collector, to the surface of which a boehmite treatment is applied, in at least one of the electrode plate for positive electrode and electrode plate for negative electrode.
2. A battery using the electrode plate for battery as cited in Claim 1.
3. The electrode plate for battery as cited in Claim 1, wherein the thickness of a thin coating formed on the current collector surface by a boehmite treatment ranges from 0.5 μm to 5 μm .
4. The battery as cited in Claim 2, where in the thickness of a thin coating formed on the current collector surface by a boehmite treatment ranges from 0.5 μm to 5 μm .
5. An electrode plate for battery characterized by using a current collector, to the surface of which a boehmite treatment is applied, in the positive electrode plate.
6. A production method of a positive electrode plate for lithium secondary battery, the method comprising the steps of: forming a chrome oxide layer on the surface of a current collector, which is formed of a metallic foil, by applying a chromate treatment thereto; applying a coating of a paste containing an electrode active material to said current collector; and drying the paste.
7. A lithium secondary battery using a positive electrode plate that is produced according to the production method as cited in Claim 6.

Fig 1

1. Electrode Plate for Positive Electrode
2. Electrode Plate for Negative Electrode
3. Separator
4. Battery Case
5. Sealing Plate
6. Gasket
7. Positive Electrode Lead
8. Negative Electrode Lead
9. Upper Insulating Plate
10. Lower Insulating Plate

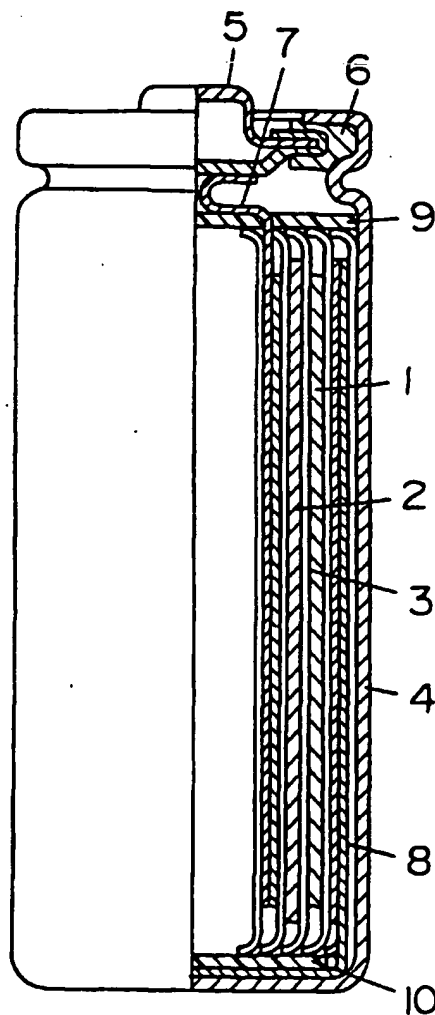


Fig 2

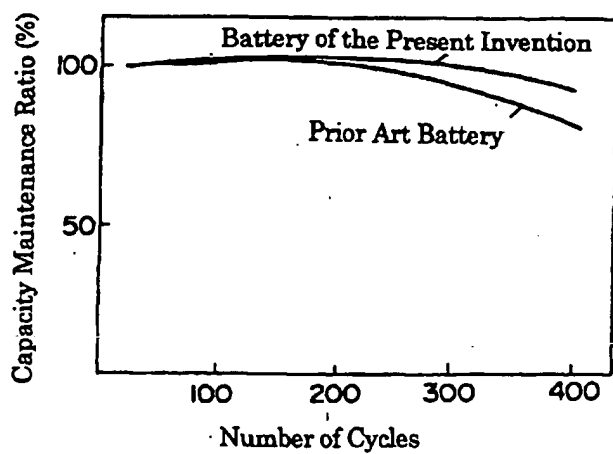
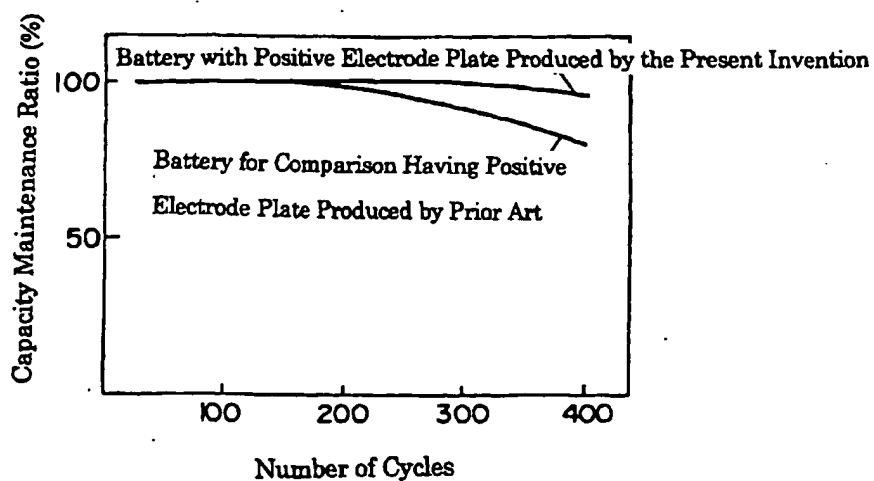


Fig 3



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP99/02828

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁶ H01M4/66, H01M4/02, H01M4/04, H01M10/40 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl ⁶ H01M4/66, H01M4/02, H01M4/04, H01M10/40 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-1999 Kokai Jitsuyo Shinan Koho 1971-1999 Jitsuyo Shinan Toroku Koho 1996-1999 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) JOIS		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 4-237955, A (Sanyo Electric Co., Ltd.), 26 August, 1992 (26. 08. 92), Page 2, column 1, lines 10 to 17 ; page 3, column 3, lines 6 to 20 (Family: none)	1-4, 7
A	JP, 1-120759, A (Sharp Corp.), 12 May, 1989 (12. 05. 89), Page 1, lower left column, lines 5 to 9, lower right column, lines 16 to 18 (Family: none)	5-7
A	JP, 9-63564, A (The Furukawa Electric Co., Ltd.), 7 March, 1997 (07. 03. 97), Page 2, column 1, lines 2 to 10 (Family: none)	5-7
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document not published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "d" document member of the same patent family		
Date of the actual completion of the international search 3 August, 1999 (03. 08. 99)		Date of mailing of the international search report 24 August, 1999 (24. 08. 99)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)